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(54) Suppression of the evolution of hydrogen sulfide gases from petroleum residua.

(57) Hydrogen sulfide gas evolution during storage or transport of petroleum residua is suppressed by the incorporation of an effective amount of certain imines and polyimines.

EP 0 405 719 A1

SUPPRESSION OF THE EVOLUTION OF HYDROGEN SULFIDE GASES PROM PETROLEUM RESIDUA

Field of the Invention

The present invention relates generally to the field of petroleum residua. More particularly, the invention relates to petroleum residua containing sulfur compounds capable of forming hydrogen sulfide gases.

Background of the Invention

A crude oil residuum or heavy oil which is often referred to as asphaltic fractions in the refining of crude oil is broadly understood to be the residue obtained from crude oil after a nondestructive distillation has removed substantially all of the volatile fractions. Refining temperatures are usually maintained below 350°C (660°F) as the rate of thermal decomposition of petroleum becomes substantial above such temperature. Residua are black, viscous materials and are obtained as a residue from atmospheric or vacuum distillation of a crude oil. They may be liquid at room temperature (generally atmospheric residua) or almost solid (generally vacuum residua) depending upon the crude oil. The organic chemical composition of residua is complex and may contain ash-forming metallic constituents and sulfur compounds, since metals and sulfur compounds of one type or another are generally present in crude oil. In residua, there are many varieties of sulfur compounds depending on the prevailing conditions during the formation thereof. The presence of the sulfur compounds in the residua gives rise to the generation of a gas having substantial portions of hydrogen sulfide gas. Residua have found extensive use as a bunker fuel oil, No. 6 fuel oil, fuel oil C, and marine fuel oil. Residua must be transported from the refinery to the points of use, such as a ship or a power generating plant. Unfortunately, during storage or such transport, hydrogen sulfide gases become liberated and give rise to a multitude of environmental problems.

Hydrogen sulfide is a very toxic gas and; thus, for safety purposes, the use of residua requires special handling. The contamination of residua with hydrogen sulfide forming substances thus presents a series of problems as the residua are stored or transported. Providing an effective chemical method for suppressing or inhibiting the liberation of hydrogen sulfide gases from residua is of considerable importance to the petroleum refining industry. Methods heretofore known for suppressing the liberation of hydrogen sulfide gases from residua suffer from the standpoint of effectiveness.

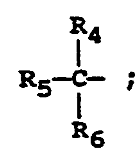
Summary of the Invention

The present invention relates generally to petroleum residua containing hydrogen sulfide gas forming substances and to a method for chemically suppressing the liberation of the hydrogen sulfide gases from such residua. The suppression or inhibiting of the generation of the hydrogen sulfide gases is accomplished by incorporating into the residua at least one oil soluble imine compound which is the condensation product of an amine or polyamine and an aldehyde or ketone in an amount sufficient to inhibit hydrogen sulfide gas evolution.

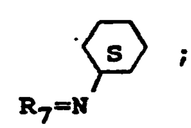
Suitable imines may be represented by the following structural formula:

$R_1(N=R_2)_x$

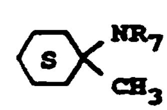
wherein x is an integer of 1-10; R_1 is independently selected from the group consisting of $R_3O(CH_2)_n$-;



cycloalkyl having 4-7 carbon atoms; phenyl, benzyl;

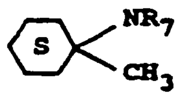


and alkyl having 1 to 20 carbon atoms or alkenyl having 1 to 20 carbon atoms; wherein R_3 is hydrogen, alkyl having 1 to 20 carbon atoms, alkenyl having 1 to 20 carbon atoms or aryl; n is an integer of 1 to 6; R_4, R_5, and R_6 are each independently selected from the group consisting of alkyl containing 1-22
carbon atoms,

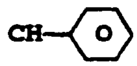


wherein R_7 is hydrogen, alkyl having 1 to 20 car-

bon atoms, and $= R_2$ with the proviso that only one of R_4, R_5 and R_6 may be

 ;

and wherein R_2 is independently selected from the group consisting of CH_2, cyclohexyl,

 ;

alkyl containing 1 to 20 carbon atoms and alkenyl containing 1 to 20 carbon atoms.

By including an imine compound of the above general structure within residua in an amount of about 10 ppm to 10,000 ppm, it is possible to suppress satisfactorily the evolution of hydrogen sulfide gases which are normally generated during the storage and transfer of the residua. Preferably, the amount of imine added to the residua ranges from about 100 ppm to about 1,000 pp.

Detailed Description of the Invention

The composition of the present invention is generally comprised of petroleum residua and an effective amount of an imine or polyimine as above-described. The imine or polyimine is incorporated in the residua after the residua are removed as a bottoms product from the refining of crude oil. The imine or polyimine should be thoroughly mixed in the residua. Thus, thorough incorporation of the imine or polyimine is preferably accomplished while the residua are at a temperature sufficiently high for the residua to have a suitable mixing viscosity but at a temperature sufficiently low to prevent thermal degradation of the additive. Often residua are too viscous at room temperature for the imine or polyimine to be conveniently dispersed evenly throughout the residua. The incorporation of the additive to suppress the evolution of hydrogen sulfide gases should be made before the residua are stored or transported.

The imine compounds useful in the present invention can be prepared by reacting a suitable aldehyde or ketone and a suitable primary amine or mixtures in a known and conventional manner. Thus, the imines can be obtained by reacting an amine with an aldehyde. The primary amine and the aldehyde are preferably combined in a mole ratio of about 1:1, i.e., the stoichiometric amount for the formation of imine with substantially no side products.

The imines and polyimines useful in the subject invention can be prepared under conventional dehydrating conditions, whereby water is removed by any suitable means. Typically, the aldehyde is added to the primary amine and the condensate recovered by mechanically separating as much of the water of reaction as possible and distilling off the remaining water. The reaction is generally exothermic and the exotherm should be controlled. The imines and polyimines can be formed from mixtures of different aldehydes or ketones and/or mixtures of different primary amines.

The amount of the imine or polyimine as herein defined effective to inhibit hydrogen sulfide gas liberation will vary, depending on various factors, for example, the particular residuum and conditions of storage and transport. In practice, at least an amount of about 10 ppm additive based on the weight of the residuum is used and preferably an amount of at least 100 ppm is used. Amounts of imine or polyimine exceeding 10,000 ppm can be employed; but, in general, there is usually no commercial or technical advantage in doing so.

Test Procedure

In the following examples, the effectiveness of the imine additives is determined by the following hydrogen sulfide gas evolution analysis. Into a metal container, the imine and 500 grams of sample residua are charged at ambient temperature. After capping the container, the container and contents therein are heated in a constant temperature bath for 60 minutes at 82 °C (180 °F). The container is then removed from the bath and shaken in a shaker for 30 seconds. Thereafter, the container and contents are again heated at 82 °C (180 °F) for another 30 minutes. Then the container and the contents are shaken again for 30 seconds. Immediately, after the second shaking, the cap is replaced with a one hole stopper. Connected to the stopper hole is a Dräger tube whose other end is connected to a Dräger gas detector pump. With one stroke of the pump, a gas sample is withdrawn through the tube. The tube is removed from the container. Thereafter, two strokes of pure air are brought through the tube allowing the absorbed hydrogen sulfide to convert quantitatively. The length of the discoloration in the tube blackened by H_2S corresponds to the hydrogen sulfide concentration in the vapor above the liquid in the container. Alternatively, the headspace gas after the second shaking can be analyzed using a gas chromatograph connected to a mass spectrometer or other suitable device for quantitatively measur-

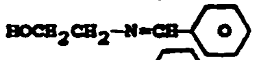
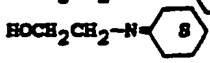
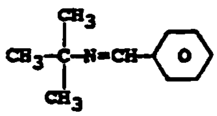
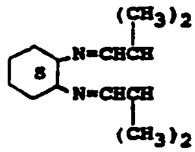
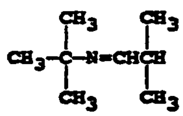
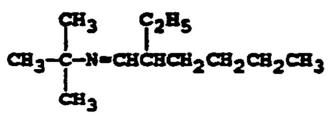
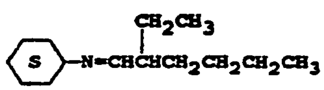
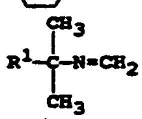
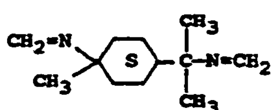
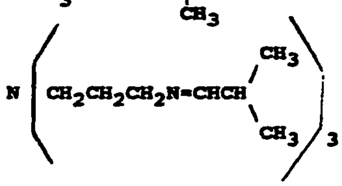
ing H_2S.

In the following examples, all percentages are given on a weight basis unless otherwise indicated.

Examples 1-12

In the laboratory, various imines at various additive levels ranging from 100 ppm and 300 ppm were tested for their efficacy to suppress the liberation of hydrogen sulfide gas in different residua using the test procedure as above described. Residuum A employed in Tests 1-3 was bottoms from a fluid catalytic cracking unit. Residuum B employed in Tests 4-12 was a marine fuel oil blend. The results of such tests are summarized in the following table:

Table

Test No.	Imine	Amount, ppm	H_2S in Head Space, ppm	% H_2S Reduction
1.	Residuum A (no additive)	—	889	—
2.		300	469	62
3.		300	782	12
4.	Residuum B (no additive)	—	1675	—
5.		300 150	<100 <100	100 100
6.		300	<100	100
7.		300 150	<100 937	100 44
8.		300 150	<100 <100	100 100
9.		300 150	141 701	92 58
10.*		300 150	592 1526	65 8
11.		300 150	441 815	74 51
12.		300 150	<100 <100	100 100

*R^1 in the compound of Test No. 10 was a branched C_9-C_{14} alkyl radical.

The imine used in Test No. 2 was obtained by stirring one mole of ethanolamine dissolved in toluene at room temperature while one mole of benzaldehyde was added dropwise. The resulting mixture was stirred an additional one-half ($\frac{1}{2}$) hour and thereafter placed in a rotary evaporator heated at 80° C under pressure of 20mm Hg to remove most of the water of reaction and to strip off the toluene. The imine product slowly precipitated as crystals.

The imine used in Test No. 3 was obtained by stirring one mole of ethanolamine dissolved in toluene at room temperature while one mole cyclohexanone was added dropwise. The resulting mixture was stirred an additional one-half ($\frac{1}{2}$) hour and thereafter placed in a rotary evaporator heated at 80° C under a pressure of 20mm Hg to remove the water of reaction and to strip off the solvent. The resulting product was a clear colorless oil.

The imine used in Test No. 5 was obtained by stirring one mole of t-butylamine while one mole of benzaldehyde was added dropwise. The resulting mixture was stirred an additional one-half ($\frac{1}{2}$) hour and thereafter placed in a rotary evaporator heated at 80° C under a pressure of 20mm Hg to remove the water of reaction and unreacted reagents. The resulting product was a clear liquid having a boiling point of 222° C at 760mm Hg.

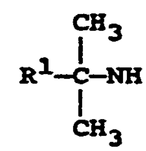
The imine used in Test 6 was obtained by stirring one mole of 1,2-diaminocyclohexane while one-half ($\frac{1}{2}$) mole of isobutylaldehyde was added dropwise. The resulting mixture was stirred an additional one-half ($\frac{1}{2}$) hour and thereafter placed in a rotary evaporate heated at 80° C under a pressure of 20mm Hg to remove the water of reaction and unreacted reagents. The resulting product was a clear liquid having a boiling point of 120° C at 20mm Hg. This product was stirred and then an additional one-half ($\frac{1}{2}$) mole of isobutylaldehyde was added dropwise. The resulting mixture was stirred an additional one-half ($\frac{1}{2}$) hour and thereafter placed in a rotary evaporator heated at 80° C under a pressure of 20mm Hg. The resulting product was a colorless oil having a boiling point of 140° C at 20mm Hg.

The imine used in Test No. 7 was obtained by stirring one mole of t-butylamine while one mole of isobutylaldehyde was added dropwise. The resulting mixture was stirred an additional one-half ($\frac{1}{2}$) hour and thereafter placed in a rotary evaporator heated at 80° C under a pressure of 20mm Hg to remove the water of reaction and unreacted reagents. The resulting product was a liquid having a boiling point of 125° C at 760mm Hg.

The imine used in Test No. 8 was obtained by stirring one mole of t-butylamine while one mole of 2-ethylhexanal was added dropwise. The resulting mixture was stirred an additional one-half ($\frac{1}{2}$) hour and thereafter placed in a rotary evaporator heated at 80° C under a pressure of 20mm Hg to remove the water of reaction and unreacted reagents. The resulting product was a colorless liquid having a boiling point of 180-185° C at 760mm Hg.

The imine used in Test No. 9 was obtained by stirring one mole of cyclohexamine while one mole of 2-ethylhexanal was stirred an additional one-half ($\frac{1}{2}$) hour and thereafter placed in a rotary evaporator heated at 80° under a pressure of 20mm Hg to remove the water of reaction and unreacted reagents. The resulting product was a dark orange oil.

The imine in Test No. 10 was obtained by dissolving 100 grams of Primene 81R, a tertiary amine obtained from Rohm-Haas, Inc. and having the formula:



wherein R^1 is a branched C_9-C_{14} alkyl radical and 41 grams of formalin (37% by weight aqueous solution of formaldehyde) in 25 grams of xylene. The resulting mixture was stirred and heated at 60° C for one hour and then transferred to a separator funnel. The aqueous layer was drawn off. The organic layer was washed twice using 25 ml of water during each washing. The organic layer was heated to distill off remaining water in the product and returning the xylene to the product. The resulting solution was a light yellow solution.

The imine used in Test No. 11 was prepared by stirring one mole of 1,8-diamino-p-menthane with two moles of formaldehyde (37% aqueous solution). Mixing was continued for two hours at 55° C. Then, 25 ml of dichloromethane was added and the resulting mixture was transferred to a separator funnel. The lower organic layer was removed. The solvent was stripped from the organic layer leaving a light orange oil.

The imine used in Test 12 was prepared by mixing one mole of tris(3-aminopropyl) amine and three moles of isobutylaldehyde in toluene and heating the mixture at reflux. Water of reaction was collected in a Dean-Stark trap. The product was then vacuum distilled and collected.

Examples 13-21

Additional imines and polyimines were prepared and tested for their efficacy in suppressing the evolution of hydrogen sulfide gases from petroleum residua.

In Test No. 13, one mole of 2,5-diaminohexane was stirred at room temperature while 2 moles of 2-ethylhexanal was added dropwise to the diaminohexane over a period of 30 minutes. After the aldehyde addition was completed, the water formed by the reaction was distilled off leaving the resulting polyimine, N,N′-2-ethyl-hexylidene-2,5-diaminohexane as a high yellow colored product. 70 ppm of the polyimine was added to a residuum of a known H_2S concentration. The percent reduction of the H_2S in the head space using the above-described procedure was determined to be 69.

In Test No. 14, one mole of mixture of the 2,2,4 and 2,4,4 isomers of trimethylhexamethylene-1,6-diamine was stirred at room temperature while 2 moles of 2-ethylhexanal was added dropwise to the diamine over a period of 30 minutes. After the aldehyde addition was completed, the water formed by the reaction was distilled off leaving the resulting mixture of polyimine, N,N′-2-ethylhexy lidene-2,2,4-trimethylhexamethylenediamine and N,N′-2-ethylhexylidene-2,4,4-trimethylhexamethylenediamine. This mixture was also effective in reducing H_2S in residua.

In Test No. 15, one mole of Primene 81R amine, as used in Test No. 10 above, was stirred while 2 moles of 2-ethylhexanal was added dropwise to the amine over a period of 30 minutes. After the aldehyde addition was completed, the water formed by the reaction was distilled off leaving the resulting imine. 70 ppm of the imine was added to a residuum of a known H_2S concentration. The percent reduction of the H_2S in the head space using the above-described procedure was determined to be 71.

In Test No. 16, one mole of bishexamethylenetriamine and three moles of 2-ethylhexanal were dissolved in xylene. The reagent were refluxed for 4 hours. Water of reaction was collected in a Dean-Stark trap. When water ceased distilling, the reaction mixture was cooled to yield a dark colored oil which was identified as N,N′-dimethylhexylidene-bishexamethylenetriamine. 70 ppm of the polyimine was added to a residuum of a known H_2S concentration. The percent reduction of the H_2S in the head space using the above-described procedure was determined to be 65.

In Test No. 17, one mole of oleylamine obtained from Armak and one mole of formaldehyde were dissolved in xylene. The reagents were refluxed for one hour. Water of reaction was collected in a Dean-Stark trap. When water ceased distilling, the reaction mixture was cooled to leave an imine having a light yellow color. Upon storage at room temperature, the imine trimerizes to form a hexahydrotriazine which, under test conditions, reverts back to the imine. 70 ppm of the polyimine was added to a residuum of a known H_2S concentration. The percent reduction of the H_2S in the head space using the above-described procedure was determined to be 70.

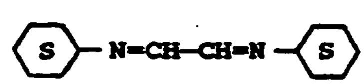
In Test No. 18, one mole of 2-aminoethylpiperazine and two moles of 2-ethylhexanal were dissolved in xylene. The reagents were refluxed for one hour. Water of reaction was collected in a Dean-Stark trap. When water ceased distilling, the reaction mixture was cooled to leave a imine, N-2-ethylhexylidene-N′-2-ethylhexenyl-2-aminoethylpiperazine, as a dark range colored oil. 70 ppm of the polyimine was added to the residuum of a known H_2S concentration. The percent reduction of the H_2S in the head space using the above-described procedure was determined to be 65.

In Test No. 19, one mole of glyoxal was added dropwise at room temperature to chloroform solvent containing two moles of n-butylamine. The resulting mixture was stirred for 45 minutes while being maintained at room temperature. The water layer was decanted from the mixture; and the solvent and remaining water were removed from the mixture by the use of a rotary evaporator heated at 80°C under reduced pressure of 20 mm Hg to yield a light yellow oil. A proton NMR spectra confirmed that the diimine of the following chemical structure was obtained:

$C_4H_9N=CH-CH=NC_4H_9$

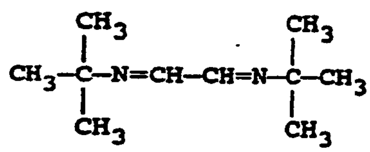
When 150 ppm and 300 ppm of the diimine prepared in accordance with Test No. 19 were added in separate tests to a residuum having a head space H_2S concentration of 10,597 ppm as determined by the above-described test procedure, it was observed that the concentration of the head space H_2S was reduced 33% and 71% in the respective tests.

In Test No. 20, one mole of cyclohexylamine was dissolved in chloroform. The resulting solution was heated to 60°C and then 0.5 mole of glyoxal was added dropwise to the solution. During the aldehyde addition, a large amount of solid formed. After 30 minutes standing, the mixture was cooled and the solid was recovered by filtration. The collected solid was recrystallized from hexane to yield a white colored needle product. A proton NMR spectra confirmed the product was a diimine of the following chemical structure:



When 100 ppm and 300 ppm of the diimine prepared in accordance with Test No. 20 were added in separate tests to a residuum having a head space H_2S concentration of 896 ppm as determined by the above described test procedure, it was observed that the concentration of the head space H_2S was reduced 70% and 77% in the respective tests.

In Test No. 21, one mole of glyoxal was added dropwise at room temperature to chloroform solvent containing two moles of t-butylamine. The resulting mixture was then refluxed for one hour, cooled and left standing overnight. A large volume of light yellow crystals formed in the flask on standing. The crystals were filtered off and dissolved in hot hexane. The hexane was removed using a rotary evaporator heated at 80°C under a pressure of 20 mm Hg to remove the water of reaction and to strip off the solvent to yield a light yellow solid. A proton NMR spectra confirmed that a diimine of the following chemical structure was obtained:



When 200 ppm of the prepared diimine was added to a residuum having a head space H_2S concentration of 1216 ppm as determined by the above-described test procedure, it was observed that the concentration of the head space H_2S in the head-space was reduced 95%.

As various changes can be made in the above described invention without departing from the scope of the invention, it is intended that the above description shall be interpreted as illustrative only and not in a limiting sense.

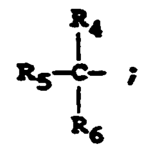
Claims

1. A process of inhibiting the liberation of hydrogen sulfide gas during storage or transport of petroleum residua containing hydrogen sulfide comprising adding to said residua or otherwise incorporating into said residua a sufficient amount of an oil soluble imine compound which is the condensation product of an amine or polyamine and an aldehyde, dialdehyde or ketone.

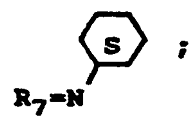
2. A process of inhibiting the liberation of hydrogen sulfide gas during storage or transport of petroleum residua containing hydrogen sulfide from a refinery comprising adding to said residua a sufficient amount of the following amine compound to inhibit hydrogen sulfide gas evolution as represented by the following structural formula:

$R_1(N=R_2)_x$

wherein x in an integer of 1-10; R_1 is independently selected from the group consisting of $R_3O(CH_2)_n$-;

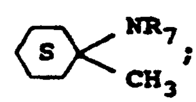


cycloalkyl having 4-7 carbon atoms; phenol, benzyl;

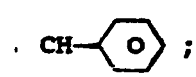


and alkyl having 1 to 20 carbon atoms or alkenyl having 1 to 20 carbon atoms; wherein R_3 is hydrogen, alkyl having 1 to 20 carbon atoms, alkenyl having 1 to 20 carbon atoms or aryl; n is an integer of 1 to 6; R_4, R_5, and R_6 are each independently selected from the group consisting of alkyl containing 1-22 carbon atoms,

wherein R_7 is hydrogen, alkyl having 1 to 20 carbon atoms, and $=R_2$ with the proviso that only one of R_4, R_5 and R_6 may be



and wherein R_2 is independently selected from the group consisting of CH_2, cyclohexyl,

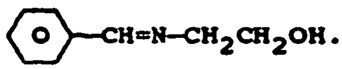


alkyl containing 1 to 20 carbon atoms and alkenyl containing 1 to 20 carbon atoms.

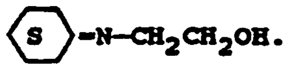
3. The process of claim 1 or 2 wherein the imine additive is present in the amount of about 10 ppm to 10,000 ppm.

4. The process of claim 3 wherein the imine addition is present in the amount of about 100 ppm to 1,000 ppm.

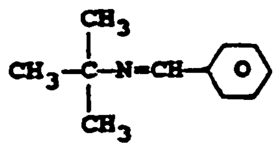
5. The process of any preceding claim wherein the imine additive has the chemical structure of:



or



or



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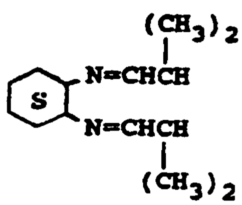

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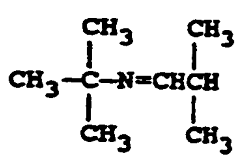

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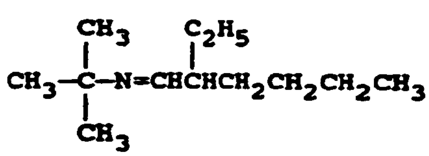

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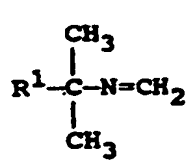
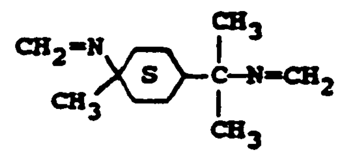


wherein R^1 is a straight or branched C_9-C_{14} alkyl radical

or



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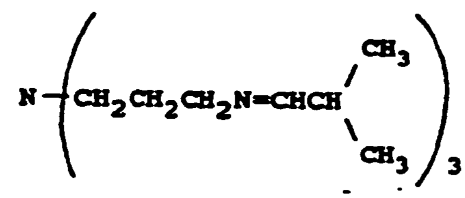
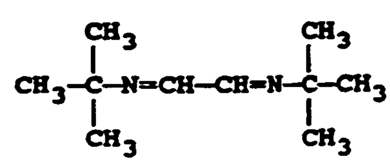


6. The process of any of claims 1 to 4 wherein the imine additive is N,N′-2-ethyl-hexylidene-2,5-diaminohexane or a mixture of N,N′2-ethylhexylidene-2,2,4-trimethylhexamethylenediamine and N,N′-2-ethylhexylidene-2,4,4-trimethylhexamethylenediamine or N,N′-dimethylhexylidene-bishexamethylenetriamine or N-2-ethylhexylidene-N′-3-ethylhexenyl-2-aminoethylpiperazine.

7. The process of any of claims 1 to 4 wherein the imine additive has the chemical structure of $C_4H_9N=CH-CH=NC_4H_9$.

or

or



8. A composition comprising petroleum residua and an oil soluble imine compound as specified in any of claims 1, 2 and 5 to 7, in an amount sufficient to inhibition hydrogen sulfide evolution from the residua.

9. The composition of claim 8, wherein the imine is present in an amount as specified in claim 3 or 4.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 4479

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 352 855 (ENIRICERCHE) * Claims 1-4,6-8 *	1-9	C 10 L 1/22 C 10 L 3/10 C 10 G 29/20 E 21 B 41/02 C 23 F 11/14
A	US-A-3 770 377 (R.M. SCOTT) * Claims 1-5 *	1	
A	US-A-2 596 425 (M.I. MOYER) * Claims 1,2; column 1, lines 37-47 *	1	
A	US-A-2 596 273 (M.I. MOYER) * Claims 1,2; column 1, lines 37-47 *	1	
A	US-A-2 701 187 (H.J. ANDRESS) * Claims 1-6 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 10 L
C 10 G
E 21 B
C 23 F
C 07 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04-10-1990	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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D : document cited in the application
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& : member of the same patent family, corresponding document